Supporting Information

Regulating the solvation structures through high-entropy strategy for wide-temperature zinc-ion batteries

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Research Methods

Materials

Acetylene black, 60% poly(tetrafluoroethylene) (PTFE) aqueous solution, zinc foil (100 μ m, 99.9%), copper foil (20 μ m), titanium foil (100 μ m), stainless steel (SS), coin cells (CR2025). Zinc bromide (ZnBr₂, 99.995%), lithium bromide (99.9%), and N-methyl-2-pyrrolidone (NMP) were purchased from Aladdin. Commercial vanadium oxide (V₂O₅) powder and sodium chloride (NaCl, 99.9%) were obtained from Macklin. Glass fiber separators were purchased from GE Whatman.

2.252 g of ZnBr₂ was dissolved in 5 ml of deionized water to produce the 2 mol·L⁻¹ ZnBr₂ electrolytes, designated as baseline electrolytes (2M ZnBr₂). 7.882 g of ZnBr₂ was dissolved in 5 ml of deionized water to produce the ZnBr₂·3H₂O electrolytes, designated as electrolytes (ZnBr₂·3H₂O). 7.882 g of ZnBr₂ and 6.080 g of LiBr were dissolved in 5 ml of deionized water to produce the Li₂ZnBr₄·9H₂O electrolytes, designated as electrolytes (Li₂ZnBr₄·9H₂O).

Preparation of Zinc Anode

Commercial zinc foil with a thickness of 100 μ m was polished with sandpaper to remove the passivation layer, washed with ethanol, and dried for 8 hours. The polished zinc foil was then cut into circular pieces with a diameter of 16 mm, to be used as the zinc anode for Zn||Zn symmetric cells, Zn||Cu asymmetric cells, and Zn||NVO full cells.

Preparation of NVO Cathode

 $NaV_3O_8 \cdot 1.5H_2O$ (NVO): 2 g of commercial V_2O_5 powder was added to 30 mL of NaCl aqueous solution (2 mol·L⁻¹). After stirring at 30°C for 96 hours, the mixture was washed several times with deionized water. The final product was obtained as a black-red powder through freezedrying.

First, 30-50 mg of a 60% PTFE aqueous solution was added to a 5 mL beaker, followed by approximately 2 mL of anhydrous ethanol, and subjected to ultrasonic cleaning for 20 minutes to disperse the PTFE uniformly in ethanol. Then, NVO and acetylene black powder were weighed according to a weight ratio of active material: conductive agent: binder = 7:2:1, and thoroughly ground in a mortar until well mixed. This mixture was added to the beaker containing the PTFE solution and subjected to ultrasonic cleaning for 1 hour, followed by drying in an oven. A small amount of ethanol was added to moisten the dried solid, which was then evenly spread on weighing paper and dried again to obtain an NVO cathode film. The film was then cut into rectangular cathodes with a side length of approximately 3 mm for batteries assembly, with a mass loading of NVO in the coin cells of 8 mg·cm⁻².

Electrochemical Testing

All batteries were assembled in an open environment and allowed to stand for 2 hours before electrochemical measurements were conducted. The electrochemical performance was tested using a LAND batteries testing system in CR2025 coin cells. Zn||Zn symmetric cells, Zn||Cu cells were assembled in an orderly manner using a negative electrode shell, spring, gasket, zinc sheet (16 mm), glass fiber separator, metal cathodes (Zn, Cu), and positive electrode shell, with a maximum electrolyte volume of 100 µL per cells. Zn||NVO full cells was assembled in an orderly manner using a negative electrode shell, spring, gasket, zinc sheet (16 mm), glass fiber (GF/A 1820) containing 80 µL of electrolyte, NVO cathode, and positive electrode shell.

Using the Zn||Zn symmetric cells, the cycling stability of zinc plating/stripping in different electrolytes at various temperatures was evaluated within a voltage range of -1.0 V to 1.0 V. To assess the Coulombic efficiency (CE) at a cutoff potential of 0.5 V, Zn||Cu cells were assembled. The cycling performance and rate capability of the Zn||NVO full cells were tested in a voltage range of 0.3 V to 1.6 V. The performance of low-temperature batteries was evaluated in a low-temperature chamber at -30°C.

Using the Autolab electrochemical workstation, cyclic voltammetry (CV) curves were obtained for the Zn||NVO batteries under the conditions of a voltage range of 0.3 V to 1.6 V and a scan rate of 0.1 mV·s⁻¹. Linear sweep voltammetry (LSV) experiments were conducted at a scan rate of 10 mV·s⁻¹, with a starting voltage of 0.5 V and a cutoff voltage of 3 V, measuring the electrochemical window curve. The ionic conductivity of different electrolytes was determined using a conductivity meter (DDSJ-318) at temperatures ranging from -60°C to 60°C. The ionic conductivity (σ) can be calculated using the following formula:

$\sigma = d / (R * S)$

where σ is the ionic conductivity, d is the membrane thickness, R is the ionic resistance, and S is the reaction area of the membrane.

The transference number of Zn²⁺ was obtained using the typical Evans method, expressed as: $t_+=I_s(\Delta V - I_0 R_0)/I_0(\Delta V - I_s R_s)$

where I_0 / I_s and R_0 / R_s are the initial/final current densities and the charge transfer resistances before and after the polarization test, respectively, and $\Delta V(10 \text{ mV})$ is the constant polarization potential during the chronoamperometric test.

Material Characterization

For the measurement of solution structure, Raman spectroscopy was collected using a Horiba Jobin Yvon Labram Aramis Raman spectrometer, with a laser (wavelength of 532 nm) operating between 3500 cm⁻¹ and 60 cm⁻¹. Six spectra were collected for each sample and integrated to achieve a high signal-to-noise ratio. Scanning electron microscopy (SEM) images were obtained at 10 kV and 15 kV using a Phenom XL-70. X-ray photoelectron spectroscopy (XPS) experiments were conducted using a Thermo Scientific K-Alpha instrument equipped with an Al K α X-ray source (1486.6 eV). The experiments were carried out in a vacuum environment of 10⁻⁸ Torr, with photoelectrons analyzed through a hemispherical analyzer. The beam spot size was 100 μ m × 100 μ m. XPS spectra were collected with an energy resolution of 0.5 eV, scanning from 0 to 1200 eV at a scan speed of 50 eV/min. Data processing included Shirley background subtraction and Gaussian-Lorentzian peak fitting, with sensitivity factors used for elemental quantitative analysis. The sample surface was subjected to chemical cleaning prior to testing and properly fixed on the sample stage to avoid charge accumulation.

MD Simulation

The simulation of the polarization force field was performed using a self-modified version of the Tinker-HP v.1.0 software package and a locally modified AMOEBA-BIO 2018 force field. The initial configuration for the simulation was generated using the amorphous cells packing tool in Materials Studio, with a density of 1 g/ml; in all cases, the density increased after volume relaxation. Slightly scaling the charges had a relatively large impact on the transport properties and improved consistency with experimental values. A variety of simulations with different sizes and compositions were prepared, and we aimed to keep the settings consistent between simulations: in the constant number, constant pressure, and constant temperature (NPT) ensemble, all simulations were conducted at a temperature of 298.15 K, with pressure controlled at 1 atm using the Berendsen method, and an integration time step of 1.0 femtosecond (fs) using the Beeman integrator; in the constant number, constant volume, and constant temperature (NVT) ensemble, all simulations were also maintained at 298.15 K using the Berendsen temperature control method, unless otherwise stated, with a reference system propagation algorithm integrator and a time step of 2.0 fs. Non-bonding interactions used a uniform cutoff of 10 Å if the box length was greater than 20 Å. Long-range corrections for van der Waals interactions were always applied. Charge interactions were calculated using the Particle Mesh Ewald method, fixing alpha at 0.386 $Å^{-1}$, with a grid of 603 points (>1 point per Å³) for the simulations of $ZnBr_2.3H_2O$ and $Li_2ZnBr_4.9H_2O$, each system containing about 2,200 water molecules, while the LiBr. $3H_2O$ simulation included 4,608 water molecules. In the LiBr.3H₂O simulation, a grid of 483 points was used, with each system containing 1,152 water molecules. The simulation of LiBr.3H₂O began with the initial geometry and evolved for 6 ns in the NPT ensemble, followed by adjusting the final configuration to match the average box size from the last 2 ns. The simulations of $ZnBr_2.3H_2O$ and $Li_2ZnBr_4.9H_2O$ started from the initial geometry and evolved for 16 ns in the NPT ensemble, with snapshots adjusted to match the average box size over the last 4 ns of the trajectory. All these simulations were executed. In the NVT ensemble, simulations were conducted for 24 ns using the readjusted box and were used for analysis. Coordinates were saved every 2 picoseconds, and the pressure stress tensor was recorded at intervals of 10 fs. After 24 ns of MD simulation, the mean square displacements of Zn^{2+} , Li^+ , water, and Br⁻ were calculated, along with the radial distribution functions and coordination numbers of Zn^{2+} with Zn^{2+} , Li^+ , water, and Br⁻.

LUMO Energy, Reduction Potential, and Br⁻/O²⁻ Exchange Free Energy

All calculations were performed at the M052X/6-311++G(3df,3pd) theoretical level and used PCM (water = 78) for implicit solvation. These calculations were carried out using Gaussian 16 rev C.01. In particular, for the reduction potential, a partial second solvation shell was added to explicitly solvate the cation or dissociated anion. A notable trend is that even with the implicit solvation model, undercoordinated ions can exhibit quite high reduction potentials. The LUMO energy and the free energy difference for the exchange of Br^-/O^2 - were directly extracted from the corresponding calculation output files. The reduction potential for the hydrogen evolution reaction requires optimization of the unaltered species, followed by sampling one of the water molecules converted into OH⁻, and then performing optimization again. The free energy of the H₂ molecule was calculated under the same theoretical level and solvation model. The expression for the reduction potential is:

$E^{red} = -[\Delta G(AOH) + 0.5\Delta G(H_2) - \Delta G(A)]/nF - 3.68$

In the equation, n represents the number of electrons, F is the Faraday constant, AOH refers to the structure of water converted to OH, and a is the structure of intact water. The Δ G term here indicates the free energy in Hartrees extracted from the calculation output files. After converting Hartrees to kcal/mol, the Faraday constant can be equivalently approximated (within rounding error) as 23.061 kcal mol⁻¹ V⁻¹. When converting Hartrees to eV, the Faraday constant can be equivalently approximated as 27.2114. A displacement of 3.68 V is used for conversion to the zinc scale, assuming the absolute voltage of the standard hydrogen electrode is 4.44 V.

Finite element simulation

The finite element modelling of Zn electrodeposition was simulated in COMSOL Multiphysics. The height of the simulation area is 30 μ m and the width is 16 μ m. The mesh is selected based on triangles or tetrahedra, while using progressively fine refinements for the electrode bands. The physical field interface was based on Tertiary Nernst-Planck and Deformed Geometry Interfaces. The transport behavior of the charged ions was described by the Nernst-Planck-Poisson equation.

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \left(-D_i \nabla c_i \right) + \nabla \cdot \left(-z_i \mu_i F c_i \nabla V \right) = R_i$$

where R_i is the electrochemical reaction source term, D_i is the effective diffusion coefficient, μ_i is the mobility (defined by the Nernst-Einstein equation), c_i is the ion concentration, $z_i = 2$ is the charge number, F is the Faraday constant, and V is the electric potential. The Bulter-Volmer equation was applied to describe the Zn plating process and the local current density was as a function of potential and ion concentration:

$$i = i_0 \left(\exp\left(\frac{1.5F\eta}{RT}\right) - \frac{c_i}{c_i^0} \exp\left(\frac{0.5F\eta}{RT}\right) \right)$$

where i_o is the exchange current density, η is the overpotential, c_i^o is the initial Zn ion concentration. The moving speed of meshes was identical to the deposition rate. To acquire the current density distribution and Zn ion flow, we configured the electrodeposition parameters of Zn to 700 s under transient conditions. The anode and cathode both have a constant potential with a potential gap of 0.27 V as the boundary condition. The ion concentration of 2.0 M was applied as the initial electrolyte boundary condition. Due to the adsorption of additives on Zn surface, the Zn plating kinetics on the additive-absorbed sites are lower than that on the additive-free sites. Therefore, the exchange current density on the additive-free surface was set as 0.218 mA cm⁻², which is higher than that on the additive-adsorbed surface with 0.14 mA cm⁻². There are other parameters including the density of Zn metal (7140 kg m⁻³), the molecule weight of Zn (65 g mol⁻¹), the simulation temperature (293.15 K), the diffusion coefficient of zinc ion (2×10^{-9} m² s⁻¹).



Supplementary Figure 1. (a) The structure of the 2M $ZnBr_2$ electrolyte predicted by MD simulations. (b) The structure of the $ZnBr_2 \cdot 3H_2O$ electrolyte predicted by MD simulations. (c) The structure of the Li₂ZnBr₄·9H₂O electrolyte predicted by MD simulations (where white represents oxygen atoms, red represents hydrogen atoms, gray represents zinc ions, brown represents bromide ions, and purple represents lithium ions).



Supplementary Figure 2. Representative configurations of $[ZnBr_{4-m}^{2-m}]_n$ (where n≤3) in $Li_2ZnBr_4 \cdot 9H_2O$ electrolytes MD simulations (where white represents oxygen atoms, red represents hydrogen atoms, gray represents zinc ions, brown represents bromine ions, and purple represents lithium ions).



Supplementary Figure 3. (a) FTIR spectra of the O-H bending vibration. (b) FTIR spectra of the O-H stretching vibration.



b Li2ZnBr4·9H2O ZnBr2·3H2O 2MZnBr2 b

Supplementary Figure 4. a, b, The images of three electrolytes at room temperature and the images of three electrolytes at -30 °C.



Supplementary Figure 5. a, Ion mobility number test for $Li_2ZnBr_4 \cdot 9H_2O$ electrolytes at 20 °C. b, Ion mobility number test for $Li_2ZnBr_4 \cdot 9H_2O$ electrolytes at -20 °C. c, Ion mobility number test for $ZnBr_2 \cdot 3H_2O$ electrolytes at 20 °C. d, Ion mobility number test for $ZnBr_2 \cdot 3H_2O$ electrolytes at -20 °C.



Supplementary Figure 6. PH polots of different electrolytes.



Supplementary Figure 7. Zn||Zn symmetrical cells based on $Li_2ZnBr_4\cdot 9H_2O$ electrolytes were treated under 1 mA cm² and 1 mA h cm²



Supplementary Figure 8. the rate performance of symmetric cells with $Li_2ZnBr_4 \cdot 9H_2O$ and $ZnBr_2 \cdot 3H_2O$ electrolytes at -30°C



Supplementary Figure 9. CE of Zn deposition/stripping in Zn||Cu half-cells with Li₂ZnBr₄·9H₂O electrolytes at -30°C under 1 mA cm² and 1 mA h cm² conditions.



Supplementary Figure 10. COMSOL simulation results of the Zn dendrite growth in $ZnBr_2 \cdot 3H_2Oand Li_2ZnBr_4 \cdot 9H_2O$



Supplementary Figure 11. The LUMO energy levels of hydrogen evolution reaction with different solvation structures calculated by DFT simulation



Supplementary Figure 12. a-f, Hydrogen evolution potentials for several common solvation structures.



Supplementary Figure 13. Electrochemical windows for different electrolytes



Supplementary Figure 14. The cyclic voltammetry (CV) curves for NVO within the $Li_2ZnBr_4 \cdot 9H_2O$ electrolytes were documented at a scan rate of 0.1 mV s⁻¹, encompassing a voltage spectrum from 0.3 to 1.6 V



Supplementary Figure 15. Capacity voltage curves of $Zn \mid \mid NVO$ cells at different currents in $Li_2ZnBr_4 \cdot 9H_2O$ electrolytes.